DESCRIPTION

LIQUID ABSORBING SHEET AND

NONAQUEOUS ELECTROLYTE BATTERY PACK

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TECHNICAL FIELD

The present invention relates to a liquid

absorbing sheet for absorbing an electrolyte solution

when such a solution leaks from a nonaqueous

10 electrolyte battery cell encased in a nonaqueous

electrolyte battery pack. The present invention also

relates to a nonaqueous electrolyte battery pack that

uses such a liquid absorbing sheet.

15 BACKGROUND ART

Battery packs are widely used that have a

plurality of primary or secondary battery cells, a

circuit board, and a battery case encasing these

components. When an electrolyte solution leaks from

20 any of the battery cells, it can corrode the wiring of

the circuit board, resulting in a conduction failure

or short circuit. To prevent such corrosion and short

circuits when leakage of the electrolyte solution

occurs, a liquid absorbing element containing an

25 absorbent capable of absorbing the electrolyte

solution is arranged in the battery pack adjacent to

or in the vicinity of the battery cell (Japanese
Patent Application Laid-Open No. 2001-351588).
Various polymer materials are used as the absorbent,
including adsorbents, gelling agents and self-swelling

5   agents. Among specific examples of the absorbents
described are polyacrylate-based water-absorbing
resins, starch/graft copolymer-based water-absorbing
resins, polyvinyl alcohol-based water-absorbing resins,
polyacrylamide-based water-absorbing resins,

10   isobutyrene-maleic acid copolymer-based water-
absorbing resins, long chain alkyl acrylate
crosslinked polymers, and polynorbornens.

One drawback of these absorbents is that they
cannot effectively absorb propylene carbonate,

15   dimethyl carbonate and other carbonate-based solvents
that are widely used in nonaqueous electrolyte battery
packs, a type of batteries that have become
increasingly used in recent years. Specifically,
these solvents are used in nonaqueous electrolyte

20   secondary cells that make lithium ion-based nonaqueous
electrolyte secondary battery packs.

The present invention addresses the above-
described problem and to that end, it is an objective
of the present invention to provide a liquid absorbing

25   sheet capable of effectively absorbing the nonaqueous
electrolyte solution used in nonaqueous electrolyte

secondary cells that make nonaqueous electrolyte

battery packs (in particular, lithium ion-based

nonaqueous secondary battery packs). It is another

objective of the present invention to provide a

5   battery pack equipped with an electrolyte-absorbing

element made of such a liquid absorbing sheet.

DISCLOSURE OF THE INVENTION

In the course of our study, the present inventors

10   have found that a resin layer obtained in a particular

manner can absorb and retain significant amounts of an

electrolyte solution, the finding leading to the

present invention. Specifically, this resin layer is

obtained by irradiating UV-rays onto a particular

15   monomer composition to polymerize the composition and

thereby make a sheet. This monomer composition

contains the following components: a monofunctional

monomer component (A) comprising a monofunctional

monomer (a) capable of forming a homopolymer that is

20   soluble in nonaqueous solvents used in nonaqueous

electrolyte secondary batteries; and a polyfunctional

monomer component (B).

Specifically, the present invention provides a

liquid absorbing sheet comprising a liquid-absorbing

25   resin layer, wherein the liquid-absorbing resin layer

is obtained by irradiating UV-rays onto a monomer

composition to polymerize the monomer composition, the monomer composition containing:

a monofunctional monomer component (A) containing a monofunctional monomer (a) capable of forming a homopolymer that is soluble in a nonaqueous solvent used in a nonaqueous electrolyte secondary battery; and

a polyfunctional monomer component (B).

The present invention also provides a nonaqueous electrolyte battery pack having a nonaqueous electrolyte battery cell, a circuit board, an electrolyte-absorbing element for absorbing an electrolyte solution in the event of electrolyte leakage from the nonaqueous electrolyte battery cell, and a battery case encasing all of the above components, wherein the electrolyte-absorbing element is formed of the above-described liquid absorbing sheet.

BRIEF DESCRIPTION OF THE DRAWINGS

Figs. 1A, 1B, and 1C are each a cross-sectional view showing a liquid absorbing sheet of the present invention.

Fig. 2 is a perspective view showing a nonaqueous electrolyte battery pack of the present invention.

Fig. 3 is a perspective view showing another

nonaqueous electrolyte battery pack of the present

invention.

Fig. 4 is a diagram illustrating an electrolyte

absorption test conducted using a model battery pack.

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BEST MODE FOR CARRYING OUT THE INVENTION

First the liquid absorbing sheet of the present

invention will be described below in more detail.

The liquid absorbing sheet of the present

10   invention can be provided in different forms. For

example, the liquid absorbing sheet may be provided as

an independent sheet formed entirely of a liquid

absorbing resin layer 1 (Fig. 1A), or it may comprise

a substrate 2 with the liquid absorbing resin layer 1

15   formed on one side (Fig. 1B). Alternatively, the

liquid absorbing sheet may include an adhesive layer 3

formed over the liquid absorbing resin layer 1 (Fig.

1C). The liquid absorbing sheet with the

configuration shown in Fig. 1C can be easily secured

20   in a battery case. The adhesive layer 3 may be formed

of any conventional adhesive. The liquid absorbing

sheet of the present invention may not include the

substrate: it may be the adhesive layer formed on one

side of the liquid absorbing resin layer (the

25   configuration shown in Fig. 1C without the substrate

2).

While the adhesive layer 3 may be formed of any conventional adhesive, it is preferably formed of a liquid absorbing resin layer that itself shows adhesion. Whether a liquid absorbing resin exhibits adhesion or not depends on its composition, as will described later. By using the adhesive layer 3 that serves both as an adhesive and as a liquid absorber, the amount of the liquid that the liquid absorbing sheet can absorb can be increased as compared to a liquid absorbing sheet using a simple adhesive layer that does not absorb a liquid. We will describe this later in the description.

Although the substrate 2 for use in the liquid absorbing sheet of the present invention may be a resin film that is impermeable to electrolyte solutions (such as a plastic film made of polypropylene or other materials), it may be a material that can absorb and retain the nonaqueous solvent, including nonwoven fabric or synthetic paper formed of plastic fibers such as polypropylene, or paper. The substrate made of such a nonwoven fabric can absorb the nonaqueous solvent at an increased rate.

The liquid absorbing resin layer 1 to form the liquid absorbing sheet of the present invention may be a polymer film obtained by irradiating UV-rays onto a particular monomer composition to polymerize the

composition and thereby make a sheet. This monomer composition contains the following components: a film-forming, monofunctional monomer component (A) comprising a monofunctional monomer (a) capable of

5 forming a homopolymer that is soluble in nonaqueous solvents used in nonaqueous electrolyte secondary batteries; and a crosslinkable, polyfunctional monomer component (B).

The monofunctional monomer component (A) for use

10 in the present invention must be a monofunctional monomer (a) that can form a homopolymer soluble in nonaqueous solvents used in nonaqueous electrolyte secondary batteries. This is because, if the monofunctional monomer component (A) is composed

15 solely of a monofunctional monomer that forms a homopolymer insoluble in such nonaqueous solvents, the ability of the resulting resin layer to absorb the nonaqueous solvent becomes insufficient. By saying "a homopolymer is soluble in a nonaqueous solvent," it is

20 meant that the weight of the homopolymer is decreased by at least 10% when 1 part by weight of the homopolymer is immersed in 30 parts by weight of a nonaqueous solvent for 24 hours at room temperature (approx. 23°C). The nonaqueous solvent is especially,

25 a mixed solvent containing at least one of dimethyl carbonate, propylene carbonate, and ethylene carbonate,

which will be described later in the description. The mixture preferably contains equal volumes of the respective solvents. The decrease in weight can be determined by comparing the dry weight of the homopolymer measured after the homopolymer has been immersed in the nonaqueous solvent and then pulled out of the solvent, with the weight measured prior to the immersion period. A 100% decrease in weight means that the homopolymer has been completely dissolved in the solvent.

The monofunctional monomer (a) is such that the difference in the solubility parameter value (*i.e.*, SP value $(J/cm^3)^{1/2}$) between the monofunctional monomer and a given nonaqueous solvent used in a nonaqueous electrolyte secondary battery to which to apply the liquid absorbing sheet preferably falls within the range of -1.0 to 8.0 and, more preferably, within the range of 2.0 to 6.5. If this difference falls outside the specified range, the homopolymer becomes substantially insoluble in the nonaqueous solvent, resulting in an insufficient ability of the resulting resin layer to absorb the solvent.

The solubility parameter is determined by the Fedors equation shown below (See, R.F.Fedors, Polym. Eng. Sci., 14(2), p147, p472 (1947)). The solubility of the monofunctional monomer in the present invention

was determined for polymerized repeating units. In the following Fedors equation, 'σ' indicates the solubility parameter, 'V' indicates the molar volume (cm³/mol) and 'E$_{coh}$' indicates the binding energy (J/mol):

$$\sigma = (\Sigma E_{coh}/V)^{1/2}$$

The monofunctional monomer (a) may be a mixture of monofunctional monomers. Given that such a monomer mixture contains n mols of a monomer (a1) with a solubility parameter value of SP1 and m mols of a monomer (a2) with a solubility parameter value of SP2, then the solubility parameter value of the monomer mixture (SP$_{(monomer)mix}$) is determined by the following equation, which is equally applied to determine the solubility parameter for monomer mixtures containing three or more monofunctional monomers:

$$SP_{(monomer)mix} = (SP1 \times n + SP2 \times m)/(n + m).$$

Specific examples of such monofunctional monomers (a) include imide acrylate (SP = 27.6), N-vinyl-2-pyrrolidone (SP = 26.2), acryloyl morpholine (SP = 25), benzyl acrylate (SP = 22.9), phenoxyethyl acrylate (SP = 22.6), N,N-diethylacrylamide (SP = 20.6),

methoxypolyethylene glycol acrylate (ethylene oxide-
added mol number (n) = 9, SP = 19.6),

methoxypolyethylene glycol acrylate (ethylene oxide-
added mol number (n) = 3, SP = 20.1),

5   tetrahydrofurfuryl acrylate (SP = 23), and

phenoxypolyethylene glycol acrylate (ethylene oxide-
added mol number (n) = 6, SP = 20.7). Of these,

benzyl acrylate, N-vinyl-2-pyrrolidone,

tetrahydrofurfuryl acrylate, and acryloyl morpholine

10   are preferred because of the high absorbability of the

film for the electrolyte solution. These monomers may

be used in combination of two or more. For the

purpose of optimizing the balance between the

absorbability of the film for the electrolyte solution

15   and the hardness of the film, it is particularly

preferred to use benzyl acrylate in conjunction with

acryloyl morpholine. In such a case, the ratio of

benzyl acrylate to acryloyl morpholine (by weight) is

preferably from 30/70 to 70/30. Acryloyl morpholine,

20   when present in excess, improves the absorbability of

the film for the electrolyte solution but makes the

film hard and susceptible to cracking.

The solubility parameter value of the nonaqueous

solvent is preferably in the range of 17 to 28 and,

25   more preferably, in the range of 18 to 23. If the

nonaqueous solvent has a solubility parameter value

that falls outside the specified range, then the
solvent, when used in a lithium battery, can cause a
decrease in the cycle performance of the battery.

Among the nonaqueous solvents for use in the

5   present invention are carbonates, including dimethyl
carbonate (SP = 17.4), propylene carbonate (SP = 20.8),
and ethylene carbonate (SP = 22.5). These carbonates
may be used either individually or in combination of
two or more. One particularly preferred nonaqueous

10   solvent is a mixed solvent (SP$_{(solvent)mix}$ = 20.2)
containing equal volumes of dimethyl carbonate,
propylene carbonate, and ethylene carbonate. Using
the solubility parameter and the amount (in the number
of mols) of each of the nonaqueous solvents used in

15   the mixture, the solubility parameter of the mixed
nonaqueous solvent can be determined in the same
manner as in the determination of the solubility
parameter of multiple monofunctional monomers used in
combination.

20   The homopolymer of the monofunctional monomer (a)
is preferably obtained by adding 0.1 to 5 parts by
weight of a UV polymerization initiator (e.g., 2-
hydroxy-2-methyl-1-phenylpropane-1-one, bis-acyl
phosphine oxide, benzophenone, and 2-

25   methylthioxanthone) to 100 parts by weight of the
monofunctional monomer (a), and irradiating the

mixture with UV rays with a wavelength of 250 to 350
nm at an energy density of 100 to 2000 mJ/cm^2 to
polymerize the monomer.

According to the present invention, the
5   monofunctional monomer component (A) preferably
contains the monofunctional monomer (a) in an amount
of at least 20mol%. If too little of the monomer (a)
is present, the amount of the nonaqueous solvent that
can be absorbed by the liquid absorbing sheet may be
10   reduced.

As long as the advantages of the present
invention are not affected, other monofunctional
monomers, such as hydroxyethyl acrylate (SP = 29.6),
acrylic acid (SP = 28.7), 2-ethylhexyl acrylate (SP =
15   18.9), and lauryl acrylate (SP = 18.7), may be added
to the monofunctional monomer component (A).

The polyfunctional monomer component (B) for use
in the present invention serves to introduce
crosslinks in the liquid absorbing resin layer 1 and
20   is preferably a monomer having two or more acrylate
residues. Examples of such monomers are hydroxyl
pivalic acid neopentyl glycol diacrylate, polyethylene
glycol diacrylate (ethylene oxide-added mol number (n)
= 14), bisphenol A diacrylate, phenyl glycidyl ether
25   acrylate, and hexamethylene diisocyanate urethane
prepolymer.

The amount of the polyfunctional monomer component (B) added to the monomer composition is such that the crosslink density preferably falls in the range of 0.0001 to 0.17 and, more preferably, in the range of 0.001 to 0.1. Too small an amount of the polyfunctional monomer component (B) may make it difficult for the liquid absorbing resin layer 1 to retain its shape, whereas too large an amount of the polyfunctional monomer component (B) may lead to an insufficient ability of the liquid absorbing resin layer 1 to absorb the nonaqueous solvent.

Given that 'a' indicates the number of the functional groups borne by a single molecule of the polyfunctional monomer, 'b' indicates the number of mols of the polyfunctional monomer present in the monomer composition, and 'c' indicates the number of mols of the monofunctional monomer present in the monomer composition, the crosslink density can be defined by the following equation:

$$\text{Crosslink density} = a \times b/(b + c).$$

The first configuration of the liquid absorbing sheet of the present invention as depicted in Fig. 1A can be obtained by coating a peelable film, such as polyethylene terephthalate film, with the above-

described monomer composition containing the monofunctional monomer component (A) and the polyfunctional monomer component (B), irradiating the coated film with UV rays to polymerize the composition

5   and thereby form a sheet, and peeling the sheet from the peelable film. The second configuration as depicted in Fig. 1B can be obtained either by coating a nonwoven fabric with the monomer composition and polymerizing the composition, or by laminating a

10   nonwoven fabric onto the first construction of Fig. 1A. The third construction as depicted in Fig. 1C can be obtained by further applying or laminating an adhesive over the liquid absorbing resin layer of the second configuration of Fig. 1B.

15   By using a peelable sheet embossed with surface patterns, the surface area of the liquid absorbing resin layer can be increased, resulting in an increase in the absorption rate of the liquid absorbing sheet.

The monomer composition containing the

20   monofunctional monomer component (A) and the polyfunctional monomer component (B) may be directly applied to the inner surface of a battery case 21 as shown in Fig. 2, rather than onto the peelable film, such as polyethylene terephthalate film. Then, by

25   irradiating with UV rays, the composition can be polymerized to form a sheet where it has been applied.

The monomer composition can be applied to the peelable sheet or nonwoven fabric by any suitable conventional technique, such as roll coater technique. The UV polymerization is typically carried out at 15 to 25°C while irradiating UV rays with a wavelength of 250 to 350 nm at an energy density of 100 to 2000 mJ/cm^2.

When the liquid absorbing resin layer itself shows adhesion (e.g., when the monofunctional monomer used in the component (A) is tetrahydrofurfuryl acrylate (SP = 23), benzyl acrylate (SP = 22.9), phenoxyethyl acrylate (SP = 22.6), phenoxypolyethylene glycol acrylate (ethylene oxide-added mol number (n) = 6, SP = 20.7), or methoxypolyethylene glycol acrylate (ethylene oxide-added mol number (n) = 3, SP = 20.1)), the construction of Fig. 1A or Fig. 1B can be directly attached to the battery pack without providing the adhesive layer. In addition, the liquid absorbing resin layer can be attached to the substrate by using a hand roller at room temperature, rather than by thermal lamination (See, Fig. 1B). Considering the fact that the leakage in many cases occurs at the cathode of the cylindrical batteries, the liquid absorbing sheet is preferably shaped as a doughnut-like shape in its plan view so that it can be applied about the cathode terminal.

According to the present invention, a flame
retardant (*e.g.*, phosphate-based liquid flame
retardant, aluminum hydroxide, and melamine cyanurate)
may be further added to the liquid absorbing resin
5   layer 1 in the liquid absorbing sheet of the present
invention. This imparts a flame retardancy to the
liquid absorbing sheet. Specifically, when a
phosphate-based liquid flame retardant is used as the
flame retardant of the present invention, it can
10   impart to the liquid absorbing resin layer 1 a flame
retardancy of grade V-0, V-1, or V-2 according to the
UL-94 standard. Furthermore, the phosphate-based
flame retardant can impart a high adhesion to the
liquid absorbing resin layer 1 since the agent remains
15   a liquid under atmospheric pressure, typically at -
13°C to 250°C, and preferably at room temperature. The
liquid absorbing resin layer 1 that shows adhesion can
be directly attached to the nonaqueous electrolyte
secondary battery pack and, thus, can eliminate the
20   need to provide an additional adhesive layer, so that
the thickness of the liquid absorbing resin layer 1
does not have to be reduced by an amount corresponding
to the thickness of the adhesive layer. Accordingly,
the amount of the nonaqueous solvent that can be
25   absorbed by the liquid absorbing sheet can be
maintained. Moreover, we have unexpectedly found that

when the phosphate-based liquid flame retardant is
used as the flame retardant of the present invention,
the insulation resistance of the liquid absorbing
resin layer 1 can be preferably maintained above 1 ×

5   10^{12} Ω even after the liquid absorbing sheet has been
subjected to a wet heat aging process (e.g., place the
liquid absorbing sheet at a temperature of 40°C under
a humidity of 90%RH for 96 hours).

Preferred examples of the phosphate-based liquid

10 flame retardant for use in the present invention
include bisphenol A bis(diphenyl)phosphate,
hydroquinol bis(diphenyl)phosphate, phenyl dixylenyl
phosphate, tricresyl phosphate, cresyl diphenyl
phosphate, trixylenyl phosphate, xylenyl diphenyl

15 phosphate, resorcinol bis(diphenyl)phosphate, and 2-
ethylhexyl diphenyl phosphate. Of these, bisphenol A
bis(diphenyl)phosphate, hydroquinol
bis(diphenyl)phosphate and phenyl dixylenyl phosphate
are preferred since they can impart high adhesion to

20 the liquid absorbing resin layer 1.

The amount of the phosphate-based liquid flame
retardant is preferably in the range of 70 to 200
parts by weight and, more preferably, in the range of
100 to 150 parts by weight with respect to 100 parts

25 by weight of the monofunctional monomer component (A)
and the polyfunctional monomer component (B) combined.

If too little or too much of the flame retardant is added, desired flame retardancy cannot be achieved.

The liquid absorbing sheet of the present invention is suitable as an electrolyte-absorbing element used in an nonaqueous electrolyte battery pack that consists of a battery case encasing nonaqueous electrolyte battery cells, a circuit board, and the electrolyte-absorbing element. The liquid absorbing sheet serves to absorb the electrolyte solution should leakage occur from the battery cell. One example of such a battery pack is shown in Fig. 2. The battery pack includes a battery case 21, which encases a circuit board 22 and a plurality of nonaqueous electrolyte battery cells 23 arranged on the circuit board 22. A liquid absorbing sheet 26 as described above with reference to Fig. 1A is arranged between the circuit board 22 and the nonaqueous electrolyte battery cells 23 for absorbing the electrolyte solution should leakage occur from any of the nonaqueous electrolyte battery cells. A metal lead 24 connects the circuit board 22 with each of the nonaqueous electrolyte battery cells 23. The metal lead 24 is also connected to external terminals 25. As shown in Fig. 3, a liquid absorbing sheet 27 as described above with reference to Fig. 1C may be arranged on top of the nonaqueous electrolyte battery

cells 23 with its substrate facing the nonaqueous electrolyte battery cells 23.

Although the battery cases of the respective nonaqueous electrolyte battery packs shown in Figs. 2 and 3 are rectangular parallelepiped with cylindrical battery cells, the shape and arrangement of the battery case and the battery cells, as well as the type of the battery cells, are not limited to those shown in the figures and may vary depending on the intended purposes of the batteries.

As set forth, the nonaqueous electrolyte battery packs of the present invention include the liquid absorbing sheet, which serves as an element for absorbing electrolyte solution should leakage of the solution occur from the battery cells. The liquid absorbing sheet achieves this function by having a liquid absorbing resin layer that can effectively absorb and retain the nonaqueous electrolyte solution. This liquid absorbing resin layer is formed of a monomer composition that contains a monofunctional monomer component (A), which comprises a monofunctional monomer (a) capable of forming a homopolymer soluble in nonaqueous solvents used in nonaqueous electrolyte secondary batteries, and a polyfunctional monomer component (B). The liquid absorbing sheet, when used in nonaqueous electrolyte

battery packs, significantly reduces the occurrence of corrosion and short circuits of the circuit board in the event of leakage of the nonaqueous electrolyte solution.

5

Examples

The present invention will now be described in detail with reference to examples.

10   Reference Example

Homopolymers formed of different monofunctional monomers were examined for their solubility in a nonaqueous solvent used in nonaqueous electrolyte secondary batteries.

15   Specifically, 1 part by weight of a photopolymerization initiator (2-hydroxy-2-methyl-1-phenylpropane-1-one (D1173, Ciba Specialty Chemicals)) was added to 100 parts by weight of a monofunctional monomer. Using a roll coater, the mixture was applied

20   to a polyethylene terephthalate film and was irradiated with a UV-ray with a wavelength of 365 nm. The UV-ray was shone at an energy density of 2000 mJ/cm^2. This caused the composition to polymerize and thereby form a polymer film. 1 part by weight of the

25   resulting film was immersed in 300 parts by weight of a mixture containing equal volumes of

dimethylcarbonate, propylene carbonate, and ethylene

carbonate (SP$_{(solvent)mix}$ = 20.2) at 23°C for 24 hours.

Subsequently, the mixture was filtrated and the solid

product remaining on the filter was dried at 100°C for

5   1 hour. The solubility (wt%) of the dried product was

determined by the equation below with the results

shown in Table 1. In the following equation, W$_1$

indicates the weight of the film prior to the

immersion period and W$_2$ indicates the weight of the

10   dried solid product:

$$Solubility = ((W_1-W_2)/W_1) \times 100.$$

(Table 1)

Monofunctional monomer	SP value	ΔSP	Solubility (wt%)
Hydroxyethyl acrylate	29.6	9.4	3
Acrylic acid	28.7	8.5	5
Imide acrylate	27.6	7.4	100
N-vinyl-2-pyrrolidone	26.2	6.0	100
Acryloyl morpholine	25	4.8	100
Benzyl acrylate	22.9	2.7	100
Phenoxyethyl acrylate	22.6	2.4	85
N,N-diethylacrylamide	20.6	0.4	100
Methoxypolyethylene glycol acrylate (n=9)	19.6	-0.6	100
Methoxypolyethylene glycol acrylate (n=3)	20.1	-0.1	100
Phenoxypolyethylene glycol acrylate (n=6)	20.7	0.5	100
Tetrahydrofurfuryl acrylate	23.0	2.8	100
2-ethylhexyl acrylate	18.9	1.3	3

15

Examples 1 through 6 and Comparative Examples 1
through 3

One of the different monofunctional monomers
shown in Tables 2 and 3, hydroxyl pivalic acid

5   neopentyl glycol diacrylate to serve as a
polyfunctional monomer and 2-hydroxy-2-methyl-1-
phenylpropane-1-one to serve as a polymerization
initiator were mixed together in the proportions shown
in Tables 2 and 3. Using a roll coater, the mixture

10 was applied to a polyethylene terephthalate film and
was irradiated with a UV-ray with a wavelength of 365
nm. The UV-ray was shone at an energy density of 2000
mJ/cm^2 to cause the composition to polymerize and
thereby form a polymer film. The polymer film was

15 peeled off from the polyethylene terephthalate film to
give a single-layered liquid absorbing sheet.

The resulting liquid absorbing sheet was immersed
in a large volume of a mixed solvent containing equal
volumes of dimethylcarbonate, propylene carbonate, and

20 ethylene carbonate ($SP_{(solvent)mix}$ = 20.2) at 23°C. After
2 hours, the appearance of the liquid absorbing resin
layer was visually examined. The liquid absorbing
sheet was pulled out of the mixed solvent and the
solvent remaining on the surface was immediately wiped

25 off. The sheet was weighed and its swell ratio was
determined. The results are shown in Table 2. Each

liquid absorbing sheet was also examined for the SP value of the monofunctional monomer ($SP_{(monomer)}$), the difference in the SP value between the monofunctional monomer and the solvent (ΔSP value), the density of crosslinks in the liquid absorbing resin layer of the liquid absorbing sheet and the state after the immersion period. The results are also shown in Tables 2 and 3.

(Table 2)

Components	Examples (wt parts)					
	1	2	3	4	5	6
Benzyl acrylate	100	100	100	—	30	100
N-vinyl-2-pyrrolidone	—	—	—	100	—	—
Acrylic acid	—	—	—	—	70	—
Polyfunctional monomer	1	0.1	10	1	1	20
Photopolymerization initiator	1	1	1	1	1	1
$SP_{(monomer)}$	22.9	22.9	22.9	26.2	27.8	22.9
ΔSP	2.7	2.7	2.7	6.0	7.6	2.7
Crosslink density	0.010	0.001	0.091	0.007	0.005	0.167
Swell ratio (times)	10	10	3	10	3	1.6
State after immersion	Film	Gel	Film	Film	Film	Film

(Table 3)

	Comparative Example (wt parts)		
	1	2	3
Benzyl acrylate	100	—	—
Acrylic acid	—	100	—
2-ethylhexyl acrylate	—	—	100
Polyfunctional monomer	—	1	1
Photopolymerization initiator	1	1	1
SP(monomer)	22.9	28.7	18.9
ΔSP	2.7	8.5	-1.3
Crosslink density	0.000	0.005	0.005
Swell ratio (times)	Dissolved	1.1	1.1
State after immersion	Liquid	Film	Film

As shown by the results of Tables 2 and 3, the liquid absorbing sheet of Example 1 swelled 10 times and still retained its film-like shape after it had swollen by absorbing the nonaqueous solvent. This implies that this liquid absorbing sheet can serve as an effective liquid absorbing element for absorbing the electrolyte solution should leakage of the solution occur from the nonaqueous electrolyte battery cells.

The results also indicate that the liquid absorbing sheets of Examples 2 through 6 each exhibits a good performance that allows the practical use of the liquid absorbing sheet as an element for absorbing the electrolyte solution. Nonetheless, the results of Example 2 indicate that the liquid absorbing sheet with a decreased crosslink density tends to become a

gel-like material, rather than retaining its film-
shape, after absorbing the nonaqueous solvent and
swelling. In contrast, the results of Examples 3 and
6 show that an increased crosslink density tends to
5   result in a decreased swell ratio. The results of
Example 4 indicate that a good result can be achieved
by using, rather than benzyl acrylate, N-vinyl-2-
pyrrolidone as the monofunctional monomer. The
results of Example 5 indicate that when a
10 monofunctional monomer whose homopolymer is insoluble
in the nonaqueous solvent is used together, the swell
ratio of the liquid absorbing sheet tends to decrease.

On the other hand, the results of Comparative
Example 1 indicate that the polyfunctional monomer-
15 free liquid absorbing resin layer dissolves in the
nonaqueous solvent and thus cannot be used as the
element for absorbing the electrolyte solution. The
results of Comparative Example 2 indicate that when
the monofunctional monomer has too large a SP value so
20 that its homopolymer is substantially insoluble in the
nonaqueous solvent, the swell ratio of the liquid
absorbing sheet becomes too small, making the liquid
absorbing sheet unsuitable for use as the element for
absorbing the electrolyte solution. The results of
25 Comparative Example 3 indicate that when the
monofunctional monomer has too small a SP value so

that its homopolymer is again substantially insoluble
in the nonaqueous solvent, the swell ratio of the
liquid absorbing sheet becomes too small, making the
liquid absorbing sheet unsuitable for use as the

5   element for absorbing the electrolyte solution.

Example 7 (Test for the ability to absorb an
electrolyte solution using a simulated battery pack)

      As shown in Fig. 4, a 7.0 cm (l) × 7.9 cm (w) ×

10   2.3 cm (h) ABS resin box 41 was obtained. A 6.5 cm

(l) × 6.5 cm (w) 100 μm-thick liquid absorbing sheet
42 prepared according to Example 1 was stuck to the
bottom of the box with a commercially available
adhesive. Three lithium ion batteries 43 were placed

15   on the liquid absorbing sheet 42, and a glass epoxy
substrate 44 as a circuit board was placed adjacent to
the batteries.

      A hole h was drilled through the side wall of one
of the batteries 43 that was in the middle of the

20   three. The electrolyte solution leaking from the hole
was allowed to be absorbed by the liquid absorbing
sheet. After drilling of the hole h, the batteries
were left for one day and night and the inside of the
battery pack was observed. It turned out that the

25   glass epoxy substrate was not wet. In addition, the
decrease in weight of the battery with the hole h

drilled in it was 2.5 g, which was equal to the increase in weight of the liquid absorbing sheet. These observations suggest that the leaked electrolyte solution was entirely absorbed by the liquid absorbing

5   sheet.

Examples 8 through 15

     One of the different monofunctional monomers shown in Table 4, polyethylene glycol diacrylate to

10   serve as a polyfunctional monomer (ethylene glycol-added mol number = 14, 14EG-A, Kyoeisha Chemical) and 2-hydroxy-2-methyl-1-phenylpropane-1-one to serve as a polymerization initiator were mixed together in the proportions shown in Table 4. Using a roll coater,

15   the mixture was applied to a polyethylene terephthalate film and was irradiated with a UV-ray with a wavelength of 365 nm. The UV-ray was shone at an energy density of 2000 mJ/cm^2 to cause the composition to polymerize and thereby form a polymer

20   film. The polymer film was then peeled off from the polyethylene terephthalate film to give a single-layered liquid absorbing sheet (210 g/m^2).

     Meanwhile, an electrolyte solution was prepared by adding lithium phosphate hexafluoride to serve as

25   an electrolyte to a mixed solvent containing equal volumes of dimethylcarbonate, propylene carbonate, and

ethylene carbonate ($SP_{(solvent)mix}$ = 20.2). 0.2ml of this electrolyte solution was added dropwise onto 0.03g of the liquid absorbing sheet and the time it took for the solution to be completely absorbed by the liquid

5 absorbing sheet was visually measured. The liquid absorbing sheet was also immersed in a large volume of the electrolyte solution at 23°C. After 3 hours, the appearance of the liquid absorbing resin layer was visually examined. The liquid absorbing sheet was

10 pulled out of the mixed solvent and the solvent remaining on the surface was immediately wiped off. The sheet was weighed and its swell ratio was determined. Furthermore, the liquid absorbing sheet was heated in a wet heat oven (40°C, 90%RH, 96hrs) and

15 was examined for the degree of swelling. The results are shown in Table 5.

In addition, a 5cm wide strip of a polypropylene nonwoven fabric (Unitika) was laminated onto either side of the liquid absorbing sheet using the hand

20 roller technique (23°C) or the thermal lamination technique (80°C). The adhesion strength was then determined on a tensile tester (TENSILON, Orientech) used in T-peel mode. Also, a 3cm wide strip of the liquid absorbing sheet was laminated onto an Ni

25 surface using the hand roller technique (23°C) or the thermal lamination technique (80°C). The adhesion

strength was then determined on a tensile tester
(TENSILON, Orientech) used in T-peel mode. The
results are shown in Table 5.

Each liquid absorbing sheet was also examined for
5   the SP value of the monofunctional monomer (SP$_{(monomer)}$),
the difference in the SP value between the
monofunctional monomer and the solvent (ΔSP value),
the density of crosslinks in the liquid absorbing
resin layer of the liquid absorbing sheet and the
10   state after the immersion period. The results are
also shown in Table 5.

(Table 4)

Components	Examples (wt parts)							
	8	9	10	11	12	13	14	15
Tetrahydrofurfuryl acrylate	100	—	—	—	—	—	—	—
Benzyl acrylate	—	100	—	—	—	—	—	—
Phenoxyethyl acrylate	—	—	100	—	—	—	—	—
Phenoxypolyethylene glycol acrylate (n=6)	—	—	—	100	—	—	—	—
Methoxypolyethylene glycol acrylate (n=3)	—	—	—	—	100	—	—	—
Methoxypolyethylene glycol acrylate (n=9)	—	—	—	—	—	100	—	—
Acryloyl morpholine	—	—	—	—	—	—	100	—
N,N-diethylacrylamide	—	—	—	—	—	—	—	100
Polyfunctional monomer	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Photopolymerization initiator	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5

(Table 5)

Components	Examples							
	8	9	10	11	12	13	14	15
(Degree of swelling) W/O wet heat process								
Dropwise addition (min)	30	100	120	40	15	15	120<	180
Immersed (times)	9.0	9.4	9.6	8.2	8.6	9.0	2.3	18
(Degree of swelling) With wet heat process								
Dropwise addition (min)	30	130	160	60	20	25	120<	200
Immersed (times)	9.0	9.2	9.0	8.1	8.5	8.5	2.0	17
Adhesion strength to nonwoven fabric								
Hand roller (kg/5cm)	0.4	0.03	0.03	0.1	0.03	0	0	0
Thermal lamination (kg/5cm)	0.7	0.03	0.03	0.1	0.03	0	0	0.3
Adhesion strength to Ni surface								
Hand roller (kg/3cm)	0.3	0.02	0.02	0.08	0.03	0	0	0
$SP_{(monomer)}$	23	22.9	22.6	20.7	20.1	19.6	25	20.6
ΔSP	2.8	2.7	2.4	0.5	-0.1	-0.6	4.8	0.4
Crosslink density	0.002	0.002	0.003	0.004	0.003	0.006	0.002	0.002
State after immersion	Film	Film	Film	Film	Film	Film	Film	Film

As shown by the results of Table 5, the liquid absorbing sheets of Examples 8 through 13 each swelled approximately 8 to 9 times after the immersion period and still retained the film-like shape after they had swollen by absorbing the nonaqueous solvent. This implies that each of these liquid absorbing sheets, while exhibiting varying absorption rates upon dropwise addition of a predetermined amount of the nonaqueous solvent, can serve as an effective liquid

absorbing element for absorbing the electrolyte
solution should leakage of the solution occur from the
nonaqueous electrolyte battery cells.

Although the liquid absorbing sheet of Example 14

5 swelled at a less swell ratio than the liquid
absorbing sheets of Examples 8 through 13, the sheet
exhibited a good performance that would allow the
practical use of the liquid absorbing sheet as an
element for absorbing the electrolyte solution.

10 While the liquid absorbing sheet of Example 15
showed a slower absorption rate than the liquid
absorbing sheets of Examples 8 through 13, it had a
good swell ratio.

The liquid absorbing sheets of Examples 8 through

15 12 each had an liquid absorbing resin layer that
itself showed adhesion, so that they did not require a
separate adhesion layer. In particular, the liquid
absorbing resin layer of the liquid absorbing sheet of
Example 8 showed superior adhesion.

20

Example 16 (Experiments a through e), Comparative
Example 4 (Experiments f through h), and Comparative
Example 5

The following components were mixed together in

25 the proportions shown in Tables 1 and 2: one of the
different monofunctional monomers shown in Tables 6

and 7, urethane acrylate (AH600, Kyoeisha) to serve as
a polyfunctional monomer, 2-hydroxy-2-methyl-1-
phenylpropane-1-one (D1173, Ciba Specialty Chemicals)
to serve as a polymerization initiator and a

5 phosphate-based liquid flame retardant or an ammonium
polyphosphate-based solid flame retardant. Using a
roll coater, the mixture was applied to a polyethylene
terephthalate film and was irradiated with a UV-ray
with a wavelength of 365 nm. The UV-ray was shone at

10 an energy density of 2000 mJ/cm^2 to cause the
composition to polymerize and thereby form a polymer
film. A flame-retardant nonwoven fabric (Japan
Vilene) was then laminated over the polymer film and
the polyethylene terephthalate film was removed to

15 obtain a double-layered liquid absorbing sheet.

Each of the liquid absorbing sheets so obtained
was tested for the flame retardancy, adhesion, swell
ratio upon absorption of the electrolyte solution and
insulating performance. The tests were conducted in

20 the following manner.

<Flame retardancy>

The flame retardancy of each liquid absorbing
sheet was evaluated according to the UL-94 standard.

25 The results are shown in Tables 6 and 7. The flame
retardancy of grade V-0, V-1, or V-2 indicates that

the absorbance sheet has sufficient flame retardancy for practical use.

<Adhesion>

A 5cm wide strip of a polypropylene nonwoven fabric (Japan Vilene) was laminated onto the liquid absorbing sheet over the liquid absorbing resin layer using the hand roller technique (23°C). The adhesion strength was then determined on a tensile tester (TENSILON, Orientech) used in T-peel mode. The results are shown in Tables 6 and 7.

<Swell Ratio>

An electrolyte solution was prepared by adding lithium phosphate hexafluoride to serve as an electrolyte to a mixed solvent containing equal volumes of dimethylcarbonate, propylene carbonate and ethylene carbonate. The lithium phosphate hexafluoride was added to a concentration of 1mol/l. The liquid absorbing sheet was immersed in the electrolyte solution at 23°C. After 3 hours, the liquid absorbing sheet was pulled out of the solution and the solution remaining on the surface was immediately wiped off. The sheet was weighed and its swell ratio was determined. The results are shown in Tables 6 and 7.

<Insulating performance>

The insulation resistance (Ω) of the liquid absorbing resin layer of each liquid absorbing sheet was determined before and after the wet heat process.

5 The results are shown in Tables 6 and 7.

(Table 6)

Components	Example 16 (Wt parts)				
	Experiment a	Experiment b	Experiment c	Exeperiment d	Experiment e
Benzyl acrylate	70	70	70	70	70
Acryloyl morpholine	30	30	30	30	30
Polyfunctional monomer	0.5	0.5	0.5	0.5	0.5
Photopolymerization initiator	0.5	0.5	0.5	0.5	0.5
Bisphenol A bis(diphenyl)phosphate	70	100	150	200	-
Hydroquinol bis(diphenyl)phosphate	-	-	-	-	100
Flame retardancy(UL-94)	V-0	V-0	V-0	V-2	V-2
Adhesion (kgf/5cm)	0.4	0.6	0.5	0.5	0.7
Swell Ratio (Times)	9	8	6	6	7
Insulating performance (Ω) (before wet heat process)	4×10^{12}	4×10^{12}	3×10^{12}	3×10^{12}	1×10^{10}
Insulating performance (Ω) (after wet heat process)	1×10^{12}	1×10^{12}	1×10^{12}	1×10^{12}	1×10^{9}

(Table 7)

Components	Comparative Example 4 (wt parts)			Comparative Example 5 (wt parts)
	Experiment f	Experiment g	Experiment h	
Benzyl acrylate	70	70	70	70
Acryloyl morpholine	30	30	30	30
Polyfunctional monomer	0.5	0.5	0.5	0.5
Photopolymerization initiator	0.5	0.5	0.5	0.5
Bisphenol A bis(diphenyl)phosphate	0	50	250	-
Ammonium polyphosphate	-	-	-	200
Flame retardancy (UL-94)	NA	NA	NA	V-0
Adhesion (kgf/5cm)	NA	NA	0.3	NA
Swell Ratio (Times)	9	9	4	-
Insulating performance (Ω) (before wet heat process)	9×10^{13}	9×10^{13}	9×10^{13}	3×10^{14}
Insulating performance (Ω) (after wet heat process)	2×10^{12}	2×10^{12}	2×10^{12}	3×10^{10}

As shown by the results of Table 6, the liquid absorbing sheets of Experiments a through d of Example 16 each had a good flame retardancy and adhesion, swelled 6 times or more, and exhibited a superior insulating performance. The liquid absorbing sheet of Experiment e had a high flame retardancy, adhesion, and swell ratio comparable to those of the liquid absorbing sheets of Experiments a through d. In fact,

the liquid absorbing sheet of Experiment e showed
higher adhesion than the other liquid absorbing sheets.
While the liquid absorbing sheet of Experiment e had
relatively low insulating performance, the fluctuation
of the insulating performance was small over the wet
heat process, proving high storage stability of the
liquid absorbing sheet.

The results of Table 7 for the liquid absorbing
sheets of Experiments f through h of Comparative
Example 4 indicate that the desired flame retardancy
may not be achieved not only when bisphenol A
bis(diphenyl)phosphate, a phosphate-based liquid flame
retardant, is not added, but also when its amount is
too little or too much. The liquid absorbing sheet of
Comparative Example 5, which used the ammonium
polyphosphate-based solid flame retardant, showed no
adhesion, and its insulation performance was
significantly decreased after the wet heat process.

Example 17 (Test for the ability to absorb an
electrolyte solution using a simulated battery pack)

As shown in Fig. 4, a 7.0cm (l) × 7.9 cm (w) ×
2.3 cm (h) ABS resin box 41 was obtained. A 6.5cm (l)
× 6.5 cm (w) 100 μm-thick liquid absorbing sheet 42
prepared according to Example 1 was stuck to the
bottom of the box with a commercially available

adhesive. Three lithium ion batteries 43 were placed on the liquid absorbing sheet 42, and a glass epoxy substrate 44 as a circuit board was placed adjacent to the batteries.

5   A hole h was drilled through the side wall of one of the batteries 43 that was in the middle of the three. The electrolyte solution leaking from the hole was allowed to be absorbed by the liquid absorbing sheet. After drilling of the hole h, the batteries

10   were left for one day and night and the inside of the battery pack was observed. It turned out that the glass epoxy substrate 44 was not wet. In addition, the decrease in weight of the battery with the hole h drilled in it was 2.5g, which was equal to the

15   increase in weight of the liquid absorbing sheet. These observations suggest that the leaked electrolyte solution was entirely absorbed by the liquid absorbing sheet.

20   INDUSTRIAL APPLICABILITY

       As set forth, the liquid absorbing sheet of the present invention includes a liquid absorbing resin layer that can effectively absorb the nonaqueous electrolyte solution used in nonaqueous electrolyte

25   secondary batteries. This makes the liquid absorbing sheet an effective liquid-absorbing element suitable

for use in nonaqueous electrolyte battery packs (in particular, in lithium ion-based nonaqueous electrolyte secondary battery packs).

A phosphate-based liquid flame retardant may be added to the liquid absorbing resin layer of the liquid absorbing sheet of the present invention. When added, the agent imparts superior flame retardancy to the liquid absorbing sheet. As a result, not only does the liquid absorbing sheet exhibit the high ability to absorb the nonaqueous electrolyte solution, which is required in nonaqueous electrolyte secondary batteries to make nonaqueous electrolyte battery packs (in particular, in lithium ion-based nonaqueous electrolyte secondary battery packs), but it also shows adhesion and superb flame retardancy. Accordingly, the liquid absorbing sheet of the present invention is suitable as a liquid-absorbing element for absorbing the electrolyte solution in nonaqueous electrolyte battery packs.